

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Rubber Compositions based on Co-Polymers of Butadiene and Acrylonitrile

We, PRECISION RUBBERS LIMITED, a British Company, of Bagworth, Leicestershire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Compositions with rubber-like properties based on co-polymers of butadiene and acrylonitrile are used in the industrial and engineering fields and, particularly in the aircraft industry, may be required to resist the action of both mineral oils and ester-based lubricants. Those compositions which only undergo moderate swelling when immersed in ester-based lubricants exhibit slight shrinkage when immersed in mineral oils. To eliminate the undesirable shrinkage a small quantity of natural rubber or non-oil resisting synthetic rubber has hitherto been added as part replacement for the co-polymer because natural rubber swells in mineral oils to a considerable extent. However, natural rubber also swells excessively in ester-base lubricants so that the modified compositions in fact, show a much greater swell in the said lubricants.

The object of this invention is to provide rubber-like compositions which will undergo smaller increase of volume when immersed in ester-base lubricants than has hitherto been possible while at the same time undergoing negligible loss of volume when immersed in mineral oils.

According to the present invention there is provided, an elastic, non-cellular, rubber-like composition based on co-polymers of butadiene and acrylonitrile wherein between 5 and 15 parts per 100 by weight of the co-polymers are replaced by polyethylene. More specifically between 10 and 15 parts per 100 by weight of the co-polymers are replaced by polyethylene.

It has been noted that the beneficial effect of the polyethylene increases as the molecular weight thereof increases and, according to a

feature of the invention a polyethylene having a molecular weight in excess of 20,000 is used.

The choice of polyethylene for blending with the co-polymers of butadiene and acrylonitrile (commonly termed "nitrile" rubber) for the purpose indicated above was based on the following considerations.

At temperatures below 60° C polyethylene is not soluble to any appreciable extent in any solvent; above this temperature its solubility in hydrocarbons and halogenated hydrocarbons rises sharply. Polar liquids such as esters, are poor solvents even at high temperatures and do not cause swelling at low temperatures.

The choice of high molecular weight polyethylene arose from the observations that the higher the molecular weight of the polyethylene which was blended with the nitrile rubber the lower the amount of shrinkage shown by the resultant vulcanised composition in mineral oil lubricants. This result is illustrated in Table I which compares Example I (based on the co-polymer alone) and Example II (based on a co-polymer/natural rubber blend) with Examples III, IV and V which are based on blends of the co-polymer with polyethylene products of increasing molecular weight.

The part replacement of the butadiene-acrylonitrile by natural rubber reduces the volume loss in mineral oil; likewise with the polyethylene replacement, and in the case of the highest molecular weight material the loss becomes a slight gain. The volume gain in ester-based lubricant is substantially increased by the use of natural rubber or low molecular weight polyethylene as a part replacement.

The use of high molecular weight polyethylene achieves the purpose and maintains the volume gain substantially unchanged.

It is noted that the hardness of the five compounds (Examples I—V) are substantially constant in the range 70 ± 4 and the values for tensile strength and elongation at break while slightly lower in the case of the compounds

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containing polythene, are satisfactorily in agreement. Likewise the volume losses on air ageing at 150° C are of the same order in the case of all five mixes.

5 Examples VI to VIII in Table II illustrate the effect of varying the concentration of polyethylene. The polyethylene used (Alkathene Q40 "Alkathene" being a Registered Trade Mark) has a higher molecular weight than in 10 the earlier Examples (approximately 40,000) and the proportion of co-polymer replaced varied from 5 to 15 parts per 100 parts. The progressive reduction of shrinkage in mineral oil is clearly shown.

15 In a rubber compound for engineering use there are other properties of importance besides its behaviour in the presence of oils. Such properties include low-temperature flexibility and recovery from deformation.

20 It has been observed (as indicated in the results recorded in Table I) that even with high molecular weight polyethylene the low temperature brittle point of the sulphur-cured vulcanisates is inferior to those containing none of this substance. The relation between molecular weight of polyethylene and its low temperature flexibility is illustrated in Table III (c.f. "Alkathene" published by Imperial Chemical Industries, April 1956, Table II 25 page 9 and Table III page 13) and the table establishes that this disadvantage is minimised by using high molecular weight polyethylene which has the lowest brittle point with the nitrile rubber.

35 By substituting furnace black for lampblack and by using dicumyl peroxide as the curing agent instead of the conventional sulphur system, the brittle point temperature is lowered to a figure comparable with that of the compound based on nitrile rubber alone. Table 40 IV gives the formulation and physical properties of such a compound (Example IX) which may be compared with Examples I and V of Table I. The tensile strength is substantially higher due to the use of furnace black and the system of curing adopted, the latter being referred to subsequently.

45 The % compression recovery recorded in Tables I and IV is not as good as Examples 50 III, IV, V and IX as in Examples I and II

(in Example III the value is the same as for Example I). We have found that this property is influenced by the method employed in mixing the compound. In the case of the compounds described in Table I the method of 55 mixing was to add the polyethylene in powder form to the softened nitrile rubber on a conventional two-roll mill along with the other compounding ingredients, as is normal practice. This procedure is referred to as method A. 60

Two alternative methods (methods B and C) have been adopted with a view to obtaining a more intimate mixture of the two polymers and Table IV illustrates the improved compression 65 recovery obtainable.

Examples IX and XII were mixed according to method A. With Examples X and XIII method B was adopted, this method comprising 70 "fluxing" and blending the nitrile rubber and polyethylene on a mill with rolls at a temperature above that of the melting point of the polyethylene, i.e. approx. 120° C, mixing of the other ingredients being subsequently carried out. With Examples XI and XIV method C was adopted. In this method the 75 polymers are "fluxed" and blended 50/50 in the same way as for method B and thereafter allowed to stand for some hours (e.g. overnight) before adding the remaining nitrile rubber and other compounding ingredients. 80

Methods B and C have the advantage of ensuring intimate mixing of the two polymers which are thereby the more readily able to be crosslinked by the dicumyl peroxide. It is 85 believed that, whereas in sulphur vulcanisation there will not be any reaction with the polyethylene but only with the nitrile rubber, the dicumyl peroxide will, in fact, react with both polyethylene and the nitrile rubber and it is 90 suggested that the improved compression recovery arises from this cause after the required degree of intimacy of the polymers has been obtained. The main advantages of method C over method B are, firstly, that not 95 all the nitrile rubber is subjected to high temperature which results in some undesirable gel formation and, secondly, that with the higher concentration of polyethylene even more intimate mixing is achieved.

TABLE I

Examples

Composition	I	II (Proportional parts)	III by weight)	IV	V
Butadiene-acrylonitrile co-polymer ("Polysar" Krynac 801) (I)	100	90	90	90	90
Natural Rubber Ribbed Smoked Sheets		10			
Polyethylene — AC grade 6A (II)			10		
— "Telcothene" 20 (III)				10	
— "Telcothene" 2 (IV)					10
Lampblack — "Magecol" 888 (R.T.M.)	50	50	50	50	50
Zinc Oxide	5	5	5	5	5
Stearic Acid	1	1	1	1	1
Cyclohexyl benzthiazyl sulphenamide	0.25	0.25	0.25	0.25	0.25
Tetra methyl thiuram monosulphide	2	2	2	2	2
Sulphur	0.6	0.6	0.6	0.6	0.6
Antioxidant-acetone-diphenylamine condensate	2	2	2	2	2
Physical Properties					
Hardness, B.S.°	67	67	74	72	72
Tensile Strength p.s.i. (V)	1880	1755	1530	1550	1565
Elongation at Break % (V)	440	370	370	365	435
% Volume change after immersion in fluids for 96 hrs. at 100° C.:—					
Mineral Oil to Ministry of Supply DERD.2472 B/O	-2.17	-0.60	-0.48	-0.12	+0.24
Mineral Oil to Ministry of Supply DERD.2479	-1.32	+0.97	+1.57	+1.43	+2.43
Ester Lubricant to Ministry of Supply DERD.2487	+6.19	+11.68	+10.92	+8.70	+6.30
% Compression recovery (VI)	81.3	82.7	81.3	77.7	74.8
% Volume loss on air ageing (48 hrs. at 150° C.)	1.08	2.15	2.07	1.80	1.94
Freeze Resistance (VII) R.A.E. Brittle Point, °C.	-45	-55	-25	-25	-25

TABLE 1—*continued*

- Notes: (I) Produced by Polymer Corporation of Canada. "Polysar" is a Registered Trade Mark.
- (II) AC grade 6A, made by Allied Chemical and Dye Corporation, New York, has a molecular weight of 2,000.
- (III) "Telcothene" (Registered Trade Mark) 20, supplied by Telegraph Construction and Maintenance Co. London, has a molecular weight of 24,000.
- (IV) "Telcothene" 2, supplied by Telegraph Construction and Maintenance Co. London, has a molecular weight of 32,000.
- (V) According to BS. 903 Part A2, 1956. Dumb-bells Type D.
- (VI) Test piece used was moulded 'O' ring, nominal dimensions: inside diameter 0.700", cross section diameter 0.154". The ring is held compressed between plates to 70% of its original thickness for 24 hours at 100° C. and then released and allowed to recover for 60 minutes at 100° C. in the free state. The final thickness is then measured. The % compression recovery is calculated as follows:

$$\frac{\text{Final thickness} - \text{compressed thickness}}{\text{Original thickness} - \text{compressed thickness}} \times 100$$

(VII) As described in Appendix I to Ministry of Supply Specification DTD. 5509.

(VIII) Vulcanisation in each Example I — V is 10 mins. at 315° F. and 30 mins. in steam at 60 p.s.i.

TABLE II

Composition	Examples		
	VI (Proportional	VII parts	VIII by weight)
Butadiene-acrylonitrile co-polymer ("Polysar" Krynac 801)	95	90	85
Polyethylene — "Alkathene" Q40 (I)	5	10	15
Lampblack	50	50	50
and suitable curing agents			
Hardness B.S.°	76	76	78
% Volume change after immersion in fluids for 96 hrs. at 100° C.:-			
Mineral Oil to Ministry of Supply DERD.2472 B/O	-1.68	-0.94	+1.05
Ester based lubricant to Ministry of Supply DERD.2487	+5.92	+6.69	+8.13

- Notes: (I) This is referred to in a publication of Imperial Chemical Industries dated 12th September, 1956, entitled "Alkathene Q40 R.N. Note. No. 18". The average molecular weight of "Alkathene" Q40 is in the region of 45,000.
- (II) Vulcanisation in each Example VI — VIII is 7 mins. at 360° F. and 30 mins. in steam at 60 p.s.i.

TABLE III

Melt Index (Grade number)	(I)	2	7	20
Melt viscosity (poises)		30,000	10,000	3,000
Number average molecular weight		32,000	28,000	24,000
Low temperature Brittle Point (°C.)	(II)	-70	-40	-30

- Note:* (I) As ascertained in a "grader" or "melt indexer" in the form of a simple extrusion plastometer with an orifice 8.1 mm long and 2.08 mm dia. when operated at 190° C. with a pressure of 3.0 kg/cm².
- (II) Temperature at which half dumb-bell specimens 12.5 m.m. by 2.5 m.m. × 1.6 m.m. have an even chance of breaking when bent quickly round a mandrel 8.0 m.m. diameter; specimens annealed at 100° C. for 10 minutes before test.

TABLE IV

Composition	Examples					
	IX	X (proportional parts by weight)	XI	XII	XIII	XIV
Butadiene-acrylonitrile co-polymer ("Polysar" Krynac 801)	90	90	90			
Butadiene-acrylonitrile copolymer ("Hycar" 1001) (I)				90	90	90
Polyethylene — "Telcothene" 2	10	10	10	10	10	10
Furnace Black — Philblack O (II)	50	50	50	50	50	50
Antioxidant — acetone diphenylamine condensate	2	2	2	2	2	2
40% Dicumyl Peroxide — "Dicup" 40C ("Dicup" is a Registered Trade Mark)	4	4	4	4	4	4
Method of mixing:—	A	B	C	A	B	C
Physical Properties						
Hardness B.S.°	70	74	73	79	80	80
Tensile Strength p.s.i.	3100	2910	3100	3470	2795	3010
Elongation at Break %	365	335	365	205	210	215
% Volume change after immersion in fluids for 96 hrs. at 100° C.:						
Mineral Oil to Ministry of Supply DERD.2472 B/O	+1.06	−0.12	+0.93	+0.12	+0.72	+0.83
Mineral Oil to Ministry of Supply DERD.2479	+5.51	+3.15	+5.07	+5.53	+4.26	+4.47
Ester Lubricant to Ministry of Supply DERD.2487	+9.18	+9.40	+9.14	+6.94	+8.43	+8.68
% Compression Recovery (III)	70.1	77.0	81.7	78.6	77.3	82.7
Freeze Resistance R.A.E. Brittle Point, °C.	−45	−40	−45	−45	−40	−40

Notes: (I) Made by B. F. Goodrich of America. "Hycar" is a Registered Trade Mark.

(II) Made by Philblack Ltd., Avonmouth, Bristol.

(III) As defined in Table I.

(IV) Vulcanisation in each Example IX — XIV is 7 mins. at 360° F. and 20 mins. in steam at 60 p.s.i.

WHAT WE CLAIM IS:—

1. An elastic, non-cellular rubber-like composition comprising essentially a butadiene acrylonitrile co-polymer and a proportion of polyethylene constituting 5 to 15% of the total weight of said copolymer and polyethylene.
2. A composition according to claim 1 wherein the polyethylene constitutes between 10 and 15% of the total weight of the copolymer and polyethylene.
3. A composition according to claim 1 or 2 in which said polyethylene has a molecular weight exceeding 20,000.
4. A composition according to any preceding claim having furnace black as a compounding ingredient.
5. A composition according to any preceding claim when cured by dicumyl peroxide.
6. A method of making a composition as claimed in any preceding claim, which method comprises mixing said co-polymers and the polyethylene at a temperature above the melting point of the polyethylene.
7. A method according to claim 6 wherein the polyethylene and a part of the co-polymers are mixed, the mixture is allowed to stand for

several hours and thereafter the remaining part of the co-polymers is added to the mixture.

8. A method as claimed in claim 6 or 7 in which other compounding ingredients are added to the mixture after said mixture has been produced.

9. A method as claimed in claim 8 as appendant to claim 7 wherein said other compounding ingredients are added to the mixture together with the remaining part of the co-polymers.

10. A composition when produced according to the method of claim 6, 7, 8 or 9.

11. A rubber-like composition as hereinbefore set forth in any one of Examples III to IX.

12. A rubber-like composition according to claim 1 when produced by mixing the ingredients according to method B or Method C as hereinbefore described.

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PROVISIONAL SPECIFICATION

Improvements in or relating to Rubber Compositions based on Co-Polymers of Butadiene and Acrylonitrile

We, PRECISION RUBBERS LIMITED, a British Company, of Bagworth, Leicestershire, do hereby declare this invention to be described in the following statement:—

Compositions with rubber-like properties based on co-polymers of butadiene and acrylonitrile are used in the industrial and engineering fields and, particularly in the aircraft industry, may be required to resist the action of both mineral oils and ester-based lubricants. These compositions undergo slight shrinkage when immersed in mineral oils and moderate swelling in ester-base lubricants. To eliminate the undesirable shrinkage a small quantity of natural rubber or non-oil resisting synthetic rubber has hitherto been added as part replacement for the co-polymer because natural rubber swells in mineral oils to a considerable extent. However, natural rubber also swells excessively in ester-base lubricants so that the modified compositions, in fact, show a much greater swell in the said lubricants.

The object of this invention is to provide rubber-like compositions which will undergo

smaller increase of volume when immersed in ester-base lubricants than has hitherto been possible while at the same time undergoing negligible loss of volume when immersed in mineral oils.

According to the present invention polyethylene is added as a part replacement for the said co-polymers. Between 5 and 20 parts per cent. by weight of the co-polymer may be replaced by polyethylene and preferably the amount is from 10 to 15 parts by weight.

It has been noted that the beneficial effect of the polyethylene increases as the molecular weight thereof increases and, according to a feature of the invention a polyethylene having a molecular weight in excess of 20000 is used.

The following table sets forth examples of compounds according to the present invention and (as a basis of comparison) one based on the co-polymer of butadiene and acrylonitrile alone and on a mixture of the co-polymer with natural rubber, the effect of mineral oils and of ester lubricants on all the compounds being detailed:—

	Examples				
	I	II	III	IV	V
Butadiene-acrylonitrile co-polymer "Polysar" Krynac 801 (R.T.M.)	100	90	90	90	90
Natural Rubber (Ribbed smoked sheets)		10			
Polythene — A.C. grade 6A			10		
— "Telcothene" 20 (R.T.M.)				10	
— "Telcothene" 2 (R.T.M.)					10
Lamp Black "Magecol" 888 (R.T.M.)	50	50	50	50	50
Zinc Oxide	5	5	5	5	5
Stearic Acid	1	1	1	1	1
Cyclohexyl benzthiazyl sulphenamide	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
Tetramethylthiuram monosulphide	2	2	2	2	2
Sulphur	0.6	0.6	0.6	0.6	0.6
Antioxidant — acetone diphenylamine condensate	2	2	2	2	2

Volume changes after immersion in fluids for 96 hrs. at 100° C.:

Mineral Oils					
to M. of S. DERD.2472 B/O	-2.17	-0.60	-0.48	-0.12	+0.24
DERD.2479	-1.32	+0.966	+1.57	+1.43	+2.43

Ester Lubricant					
to M. of S. DERD.2487	+6.19	+11.68	+10.92	+8.70	+6.30

A.C. Polythene Grade 6A * has a molecular weight averaging 2000					
"Telcothene" Grade 20 **	"	"	"	24000	
"Telcothene" Grade 2 **	"	"	"	32000	

* made by Allied Chemical & Dye Corporation, New York.

** supplied by Telegraph Construction and Maintenance Co. Ltd., London.

Example I is the co-polymer alone, Example II is the co-polymer with natural rubber, and Examples III, IV and V are the co-polymers with polyethylene (polythene) of increasing molecular weight.

- 5 The part replacement of the butadiene-acrylonitrile by natural rubber reduces the volume loss in mineral oil; likewise the polyethylene and in the case of the highest molecular weight material the loss becomes a slight gain. The volume gain in ester based lubricant is substantially increased by the use of natural rubber or low molecular weight polyethylene as a part replacement.
- 10 The use of high molecular weight polyethylene achieves the purpose and maintains the volume gain substantially unchanged.
- 15 Whereas our table above indicates the use of a sulphur-vulcanising recipe it is possible also to employ an organic peroxide such as dicumyl peroxide to bring about cure; such a system is believed to cross-link the polyethylene to the butadiene-acrylonitrile polymer and furthermore imparts improved low temperature resistance.
- 20 While, in general, satisfactory results are obtained by mixing polyethylene in powder form as a normal compounding ingredient, the preferred method is to band it on the roll of a hot mill and add to it progressively and in small quantities the premilled butadiene-acrylonitrile rubber.
- 25

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